UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OPTIMIZATION AND EXTRACTION OF RARE EARTH METAL IONS BY POLY (*N - METHYlHYDROXAMIC* ACID) RESIN

SECKIN BALCl

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By

SECKIN BALCI

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TABLE OF CONTENTS

Page

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science.

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SECKIN BALCI

May 1998

Chairman: **Associate Professor Md Jelas Haron, Ph.D.**

Faculty: **Science and Environmental Studies**

Poly(*N*-methyl hydroxamic acid) resin was synthesized from crosslinked poly(methacrylate-divinyl benzene). The optimum amounts of *N*-metylhydroxylamine hydrochloride, NaOH, poly(methacrylate) were 2.2 g, 4 g and and 4 g, respectively and 20 ml water-ethanol solution (75%) was used. The reaction was completed at room temperature, for 24 hours. The abilities of poly(*N*-methylhydroxamic acid) resin and poly(*N*-unsubstituted hydroxamic acid) resin to form complexes with Cu ion were compared. Kinetics study carried out indicated that metal sorption process by the resin is fast and it is suitable to be used in column technique. The resin showed good stability in buffer pH 4 and 1M HCl solution. Metal sorption capacities were determined for Cu, Fe, Y, La, Ce, Sm, Yb, Nd, Pr, Dy and Gd. Separations of Cu / Fe, Y / Sm, Y / Nd, Sm / La have been carried out.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keparluan untuk ijazah Master Sains.

PENGOPTIMUMAN SINTESIS DAN PENGEKSTRAKAN ION LOGAM NADIR BUMI OLEH POLI(ASID *N*–METIL HIDROKSAMIK) RESIN

Oleh

SECKIN BALCI

May 1998

Pengerusi: Profesor Madya Md Jelas Haron, Ph.D.

Fakulti: Sains dan Pengajian Alam Sekitar

Resin poli(asid *N*–metil hidroksamik) telah disintesis daripada poli(metakralik–divinil benzena) berangkai silang. Jumlah optimum *N*–metilhidroksilamina hidroklorida, NaOH, poli(metakrilat) adalah masing – masing 2.2 g, 4 g dan 4 g dan 20 ml larutan air – etanol (75 %) digunakan. Tindak balas dilakukan pada suhu bilik selama 24 jam. Keupayaan resin poli(asid *N*–metilhidroksamik) and poli(asid hidroksamik) untuk membentuk kompleks dengan ion Cu dibandingkan. Kajian kinetik menunjukkan bahawa proses serapan logam oleh resin adalah pantas dan sesuai untuk digunakan dalam teknik turus. Resin menunjukkan kestabilan yang tinggi dalam larutan penimbal pH 4 dan larutan 1 M HCl. Muatan erapan logam ditentukan untuk Cu, Fe, Y, La, Ce, Sm, Yb, Nd, Pr, Dy dan Gd. Pemisahan, Cu / Fe, Y / Sm, Y / Nd, Sm / La juga dilakukan.

CHAPTER I

INTRODUCTION

The phenomenon ion exchange which usually involves either inorganic or organic ions in predominantly aqueous solutions is a process involving the reversible exchange of ions in solution with ions taken by a solid ion – exchanging material without perceptible permanent change in the structure of the solid. Therefore, ion exchange can be any material that has the ability to uptake ionic species from a solution with the simultaneous release of a chemically equivalent number of ions into solution.

The importance of the ion exchange however, is coming from its widely used area that provide the highest exchange capacity and is of greatest interest in the laboratory as well as in industrial applications. They are used in many chemical processes, including simple or chromatographic separations, catalysis and analytical chemistry. Ion exchange processes are also employed in hydrometallurgy and metal recoveries, the manufacture of sugar, in pharmacy and medicine as well as in biochemistry and biotechnology, agriculture and food processing.

Within the framework of enriching economic and commercial activities among the companies and countries, the current trend of these activities

influences the chemical industry and their researches. Scientists and researchers have concentrated on some segments of chemical industry which are more commercial as well as with scientific concerns. One of these segments is the production of ion exchanger which is used in certain sectors such as nuclear technology, electroplating industry, the sweetener industry, pharmacy, medicine, biochemistry, biotechnology, analytical chemistry, homes, laboratories and small industries, water treatment, treatment of drinking water and metal recovery.

Ion exchangers have been distributed commercially under various trade names: Allasion, Amberlite, Chempro, De-Acidite, Diaion, Dowex, Duolite, Imac, Ionac, Kastel, Katex/Anex, Lewatit, Liquonex, Mykion, Permutit, Purolite, Varion, Vionit, Wofatit, Zeo-Karb, Zerolit. Functional groups for some of these ion exchangers are given in Table 1 (Dorfner, 1991).

Although hydroxamic acid ion exchange resin is still not commercially available today, many researches have been concentrated on this type of resin, especially on the various synthesis methods, within the last few years. A successful experiment to produce hydroxamic acid resin was achieved in 1965 where it was formed from a commercial carboxylic acid by esterification and then treatment with hydroxylamine. The product was confirmed with visual tests through the formation of complex by vanadium (V) and iron (III) ions. Furthermore, infrared spectrometry also confirmed the presence of hydroxamic acid groups in the product. However, the conversion of carboxylic group to hydroxamic was found to be very poor (only 3.9 %) (Petry et al., 1965).

Table 1: Functional Groups of Some Commercial Ion Exchange Resins

Functional Group	Commercial Name
Tertiary amine	Duolite A 303, Lewatit AP 49, Lewatit MP 62
Quaternary ammonium	Duolite A 132, Duolite A 161, Duolite A 162
Amidoxime	Duolite ES 346
Carboxylic acid	Duolite C 433, Duolite C 464, Duolite 468
Mercaptane	Duolite ES 465
Sulfonic acid	Duolite C 20, Duolite C 225, Duolite C 204 F
Amino–diacetic acid	Dowex A 1, Chelex 100, Amberlite IRC 718
Carboxymethyl	Serva CM 23, Serva CM 32 Serva CM 52
Diethylaminoethyl	Serva DEAE 23 SH, Serva Serva DEAE 23 SN, Serva DEAE 23 SS

Earlier two similar methods were used to synthesis this type of resin. In one method, carboxylic acid was first converted into the acid chloride and then used to produce the (hydroxamic acid) resin. The product was a bifunctional cation exchanger with carboxylic acid and hydroxamic acid (Cornaz et al., 1957). In the other method, a linear hydroxamic acid resin was produced by hydroxylaminolysis of poly (methyl acrylate) and hydroxylamine in the presence of sodium methoxide and benzene (Kern and Shulz, 1957). These explorations of synthesis of (hydroxamic acid) resin indicated that the synthesis method could be improved by using a methacrylic acid – methylacrylate copolymer as this would prevent the formation of a hydride. A series of synthesis methods were studied by using cross–linked polymer and commercial carboxylic acid as a starting material and then used for the column operation. The resin synthesized still contained carboxylic acid groups because of the difficulty in formation of the acid chloride intermediate (Vernon and Eccles, 1975).

Mandez and Pillai (1990) prepared the resin from styrene maleic acid copolymer via the four step reactions through the formation of carboxylic acid and acid chloride.

The (hydroxamic acid) resin was also synthesized by a one-step reaction by Wan Yunus (1980). The resin, which was in microporous microbead particles, was shown to be effective in the kinetics of metal sorption. The same method of one step reaction was also examined with different starting chemicals were poly(ethyl acrylate–divinyl benzene) (Wan Yunus et al., 1988 and Lee and Hong, 1994) and poly(methyl acrylate–divinyl benzene) (Haron et al., 1994).

The resins were used to separate nickel from cobalt and for iron (III) –copper-cobalt separation (Haron et al., 1994), gold from silver (Vernon and Wan Yunus, 1981), zinc from cadmium and, cobalt from copper and nickel (Shah and Devi, 1987) and uranium from neodymium (Mohammed, 1987). The resins had also been successfully used for the recovery and separation of uranium and iron from the simulated synthetic and real sea water (Vernon and Shah, 1983; Vernon and Eccles, 1976b).

Three different hydroxamic acid resins which are *N*-methyl, *N*-phenyl and *N*-unsubtituted were prepared from a commercial poly(styrene–divinyl benzene) Amberlite (XAD–4) and their properties were compared (Phillips and Fritz, 1982).The resins showed good stability and the capacities were not affected by treatment with 2 M hydrochloric acid or 1 M ammonium hydroxide. (*N*-methylhydroxamic acid) resin was synthesized by substituting *N*-methylhydroxylammonium chloride via a four step reaction. The (*N*-methylhydroxamic acid) resin was found to have the highest metal capacity and formed the most stable complexes with copper, aluminum, and thorium metal ions. The extractions of nineteen metal ions including rare earth such as europium and lanthanum were studied by using (*N*-methylhydroxamic acid) resin. The results showed, the resin extracted 50 % of the ions at different pH values. This indicate that the poly(*N*-methyl hydroxamic acid) resin can be used to separate rare earth metal ions. However, the product still contained carboxylic acid (Phillips and Fritz, 1982).

Wan Yunus et al. (1986) described an alternative method of preparing the poly(*N*-methyl hydroxamic acid) resin by hydrolysing poly(carboxylic acid-divinyl benzene). The preparation reaction was completed in 2 steps. In this study, poly(methacrylate) was used as a starting polymer to prepare poly(*N*-Methyl hydroxamic acid) resin. It was reported that the highest hydroxamic acid capacity was obtained from poly(methacrylate). Thus capability of (*N*-methyl hydroxamic acid) resin to sorb metal ions could have been increased by appropriate method and starting polymer.

The aims of this study are to synthesis a chelating polymer containing (*N*–methylhydroxamic acid) as a functional group from cross-linked poly(methylacrylate–divinyl benzene), to compare the performance of (*N*–unsubstituted hydroxamic) and (*N*–substituted hydroxamic acid) ion exchange resins, to determine the ability of the resin to sorb rare earth metal ions which are great economic important and copper and iron which are contained in the natural or industrial sources and to separate several rare earth metal ions, and copper from iron by the resin.

CHAPTER II

LITERATURE REVIEW

Ion Exchange and Chemistry

Ion exchangers is the name given to insoluble electrolytes containing labile ions that easily exchange with other ions in the surrounding medium without any major physical change occurring in the electrolytes' own structure. The process taking place is usually called the ion exchange reaction and the labile ions in the ion exchangers exchange reversibly. The ion exchanging electrolyte is in general of a macromolecule of complex nature. Since after dissociation, all electrolytes exist only as either cations or anions, the ionic sites present in a macromolecular matrix in the case of ion exchangers can also only be either cationic or anionic. Thus the different matrices consisting of repeating units in the macromolecules, such as inorganic materials, highly complex organic materials of natural origin, and the comparatively simple-structured synthetic resins, carry an electrostatic charge in the form of a surplus charge or a fixed ion which is neutralized by the charge of the labile ion. These counter ions are cations in a cation exchanger and anions in an anion exchanger.

The term ion exchange has often been closely related to or even used synonymously with adsorption and absorption. Exchange-adsorption was used instead of ion exchange during the transition in understanding from base exchange to modern cation exchange or anion exchange. It is important first to distinguish between absorption and adsorption before one can identify ion exchange.

Absorption refers to a uniform penetration of the component of a system into the solid absorbing material following the old chemical rule of "*similia similibus solvuntur* " (like likes like) and with no change in concentration. Absorption is thus a process in which the solid engulfs another substance by distributing it very evenly throughout its own entire structure. The term adsorption on the other hand refers to the interaction of a solute with a solid adsorbent through physical forces associated with the solid, resulting in a change in concentration of, e.g., a particular dissolved component of a system which occurs mainly at the surface of the solid. Adsorption is thus characterized by an increase in concentration, which takes place at the interface of the liquid carrying the solute and the solid adsorbent. Adsorption and absorption can be denoted as sorption processes. Here, although the term adsorption for an ion exchange process may appear strange, phenomena associated with ion exchange have involved mechanisms other than the ionic exchange of ions.

Today, the term ion exchangers denotes insoluble polymeric or macromolecular substances with fixed ions. The reactive groups are dissociable and either present by nature in a naturally occuring exchange material or have

later been incorporated during the manufacture of a synthetic ion exchanger. Ion exchangers are therefore reactive polymers or reactive macromolecules, but this term does not include macro-ions. In the case of ion exchangers as reactive polymers, the reactive groups are not functional, neither in the sense of the definition of functional groups in organic chemistry nor as defined in polymer chemistry. It is by reactions of polymers that ion exchangers can usually easily be obtained, and these are then called reactive polymers. The fixed ions or reactive ionic groups of ion exchangers have the ability of undergoing ionic exchange reactions, but they are also able to store ionic species as counter-ions.

Ion exchange is a phenomenon or process involving the reversible exchange of ions in solution with ions held by a solid ion-exchanging material, in which there is no directly perceptible permanent change in the structure of the solid. An ion exchanger can be any material that has the ability to uptake ionic species from a solution with the simultaneous release of a chemically equivalent number of ions into this solution. These materials include cellulose, dextran and agarose derivatives, clays and clay minerals, materials based on coal and other organic natural products, synthetic liquid ion exchangers and ion exchange membranes. While all the types just mentioned are of greater or lesser utility, in special applications, in this text by 'ion exchanger' is meant synthetic ion exchange resin, if not otherwise stated.

Types of Ion Exchangers

Ion exchange was first investigated with inorganic materials and found some industrial use, but were almost completely displaced by synthetic ion exchange resins. The demand for ion exchange materials that would satisfy the most diverse requirements led to the development of new products, which must be considered as separate ion exchanger types according to their special properties.

Among the available types, synthetic ion exchange resins are of the greatest importance. But inorganic ion exchangers should not be neglected, since these have once again aroused interest because of their mechanical, thermal and chemical properties and because, in light of their mineralogical parallels, they offer information about numerous processes in soil science. The cellulose ion exchangers represent a separate type with their own characteristics related most closely to another group. Both types have been rapidly accepted in ion exchange chromatography where they have become indispensable for analytical as well as preparative work. In addition, ion exchangers based on carbon have been produced and, together with a number of other materials with ion exchanging properties, have been investigated for their applicability. Liquid ion exchangers, as another type, probably are important primarily because of the technological possibilities they offer.

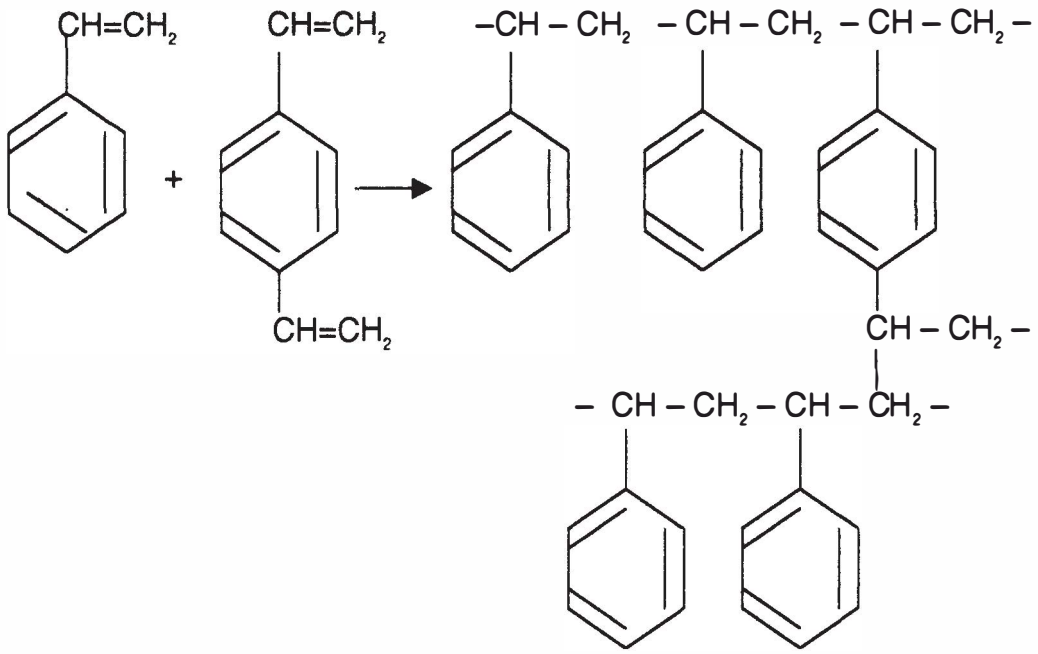
Synthetic Resin Ion Exchangers

For the description of properties of synthetic ion exchange resins, three factors are decisive: The raw material which is used for the construction of the skeleton or the matrix, bridging agents for crosslinking and insolubilization, and the type and number of the ionogenic groups. Synthetic ion exchange resins chemically are insoluble poly-electrlytes with a high but not unlimited moisture regain capacity. With regard to their function one speaks of cation exchangers, anion exchangers, and chelating ion exchanger types.

In principle, polymerization and polycondensation can in principle be used as the synthesis routes to form the matrix. At the present time, polymerization resins have become more important than polycondensation resins, as they have a higher chemical and thermal stability.

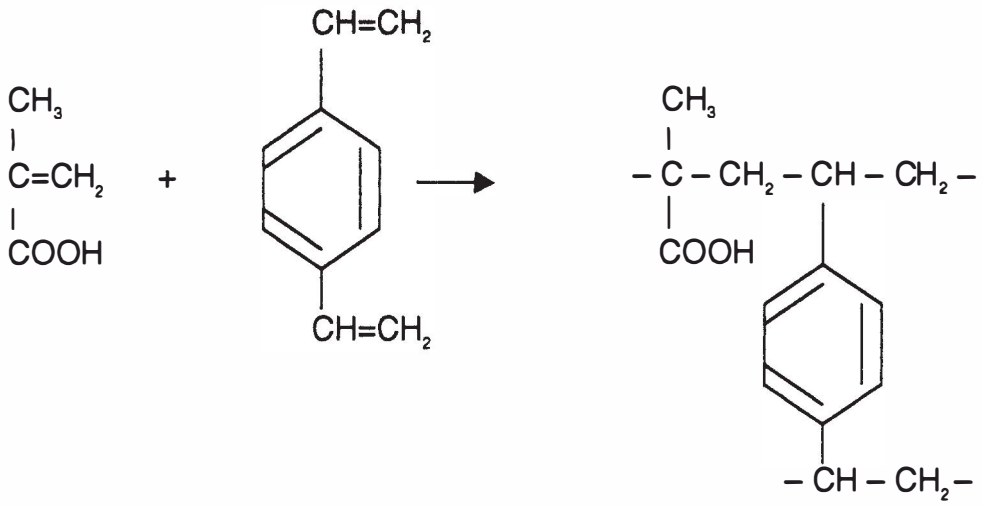
Cationic and Anionic Ion Exchange Resin

One of the most starting material is styrene which is polymerized with itself and with divinylbenzene into a polymeric molecule:

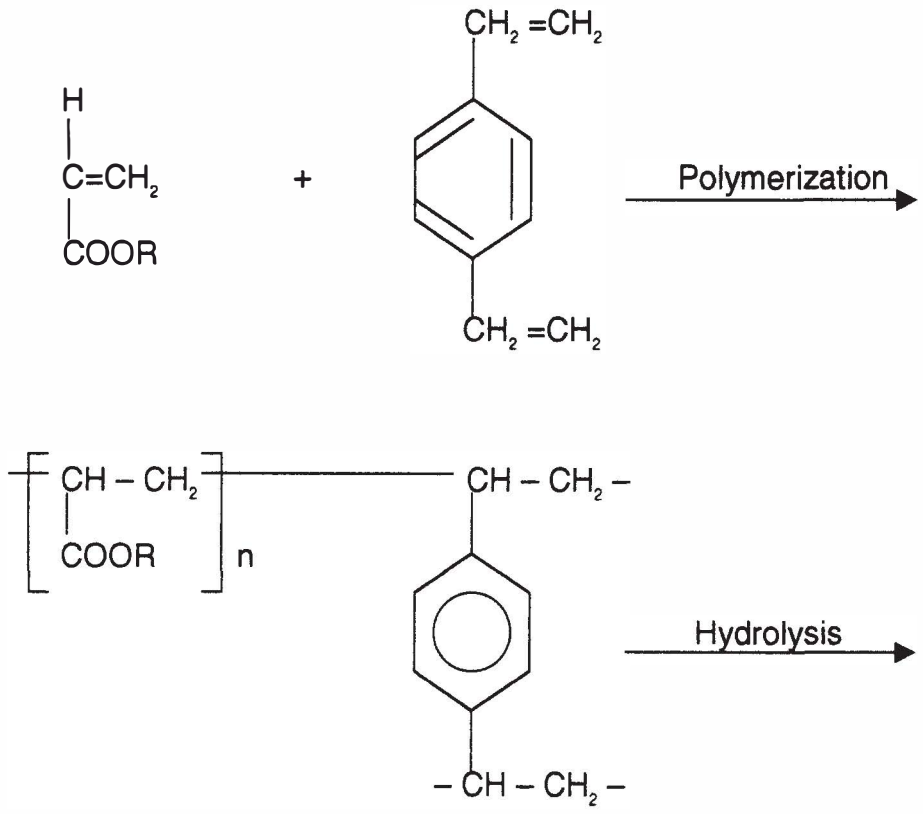


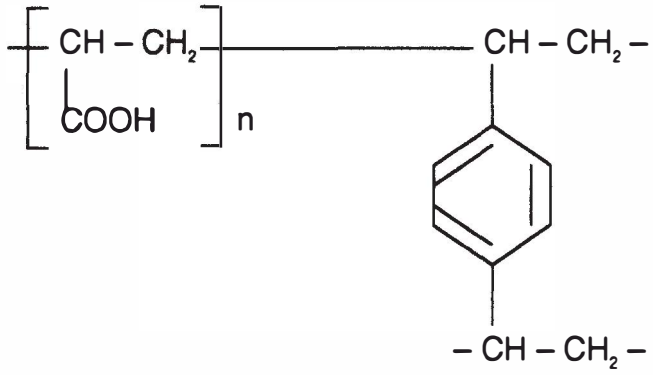
Incorporation of functional groups such as -SO_3H, -COOH and -PO_3H into the pendant benzene rings in the matrix produce a cationic ion exchange resin. Where else anionic exchange resin is produced when functional groups such as -NCH_3OH, -NH $(CH_2)_2$OH or -NH_3OH is incorporated into the benzene rings.

Another important starting materials for ion exchanger are acrylic compounds such as acrylic acid, methacrylic acid, acrylic acid ester or acrrylonitrile. For example acrylic ion exchange resins was made by suspension polymerization of methacrylic acid and divinyl benzene according to the following equation (Dorfner, 1991):



A similar ion exchanger can also be synthesized from an acrylic ester followed by hydrolysis of the copolymer (Dorfner, 1991)





A resin prepared from an acrylic molecule eleminates same interaction of an aromatic matrix, as in the resin prepared from styrene, especially with the sample containing an aromatic components.

The degree of homogeneity of ion exchange structures depends on the purity, nature and properties of the starting materials used for their production, as well as on optimum conditions of polymer synthesis. In spite of irregular structure of the matrix it is possible to produce ion exchangers with a uniform distribution of the ionic groups. The ever–increasing experimental data of recent years suggests that the heterogeneity of ion exchangers is still a different nature, and at the molecular level of polymer chemistry it is basically associated with the structure of initial copolymer.

Cross-linking naturally depends first of all on the quantity of divinylbenzene used as the cross-linking agent in production. Commercial ion exchangers of the gel type contain nominally between 2 and 12% divinylbenzene (Dorfner, 1991).